**THE MECHANISMS OF Fe(acac)$_3$ AND Cu(O$_2$CCH$_2$CH$_2$CH$_2$C$_6$H$_{11}$)$_2$
CATALYZED OXIDATION OF TETRAHYDROCARBAZOLE. IMPLICATIONS FOR
THE LONG TERM STORAGE STABILITY OF MIDDLE DISTILLATE FUELS.**

By

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INTRODUCTION

        Pedley et al.[1,2] have recently implicated alkylindoles
in the chemical reactions which are responsible for the
promotion of sediment and color body formation in an unstable
diesel fuel (90% North Sea derived straight run/ 10%
catalytically cracked) during sixteen months of ambient
storage. In addition, Dorbon and Bernasconi[3] have monitored
the change in relative concentration of nitrogen compounds
(indoles, carbazoles, and anilines) in four different LCO's
upon aging (ASTM D4625: 43°C/12wks) and have reported the
relative concentration of alkylindoles decreases to the·
greatest extent during aging.
        Control of sediment and color body formation in unstable
middle distillates during ambient storage has become an
intractable problem. For example, it has been reported that
two different commercial additive packages (composed of
antioxidant, dispersant and metal deactivator) were
ineffective in stabilizing two different unstable diesel
fuels during ambient storage[1]. The stabilization of middle
distillates by catalytic hydrogenation to remove problematic
indole nitrogen compounds is generally expensive owing to the
high temperature and hydrogen pressure needed to effect
denitrogenation[4].
        It is our belief that the ineffectiveness of commercial
additive packages to sufficiently stabilize unstable diesel
fuels during ambient storage is due to lack of understanding
of the complex and fundamental chemistry involved in fuel
oxidation. Consequently, we have initiated a research program
directed at providing a greater understanding of the
chemistry involved in low temperature middle distillate
oxidation[5]. Herein, we report results of a model study of the
Fe(acac)$_3$ and Cu(O$_2$R)$_2$ catalyzed oxidation of
tetrahydrocarbazole (I, Figure 1), a representative
alkylindole.

RESULTS AND DISCUSSIONS

In 1939, Beer et al.[6] reported that while trying to recrystallize various tetrahydrocarbazole derivatives, good yields of tetrahydrocarbazole hydroperoxide derivatives were isolated. In 1950, Beer et al.[7] reported that the structure of these hydroperoxides were that of the corresponding 1,2,3,4-tetrahydro-11-hydroperoxycarbazolenines (II,Figure 1). Subsequent studies revealed that the facile autoxidation of tetrahydrocarbazole derivatives is a general phenomenon and that the mechanism of this process involves a classical peroxyl radical chain[7,8]. Beer et al.[7] and Witkop[9], have also reported that in the presence of reducing agents or alkoxide, tetrahydrocarbazole hydroperoxides (THCHP) (II, Figure 1) are converted into the corresponding 1,2,3,4-tetrahydro-11-hydrocarbazolenine which can rearrange to the corresponding spiro-[cyclopentane-1,2'-ψ- indoxyl] (compound III,IV, respectively, Figure 1). In addition, Witkop and Patrick[9] have reported that in the presence of polar solvents or acids, THCHP rearranges to 8,9-benzcyclononadi-2,7-one (V, Figure 1).

We have confirmed all of the above mentioned results and wish to emphasize that in the presence of a suitable chain breaking-donor (CB-D) antioxidant (BHT, Vitamin E, etc.) solutions of tetrahydrocarbazole are oxidatively stable. However, when trace amounts of either $Cu(O_2CCH_2CH_2CH_2C_6H_{11})$ or $Fe(acac)_3$ are added, THC is slowly oxidized (in the presence of CB-D antioxidants).

Based upon TLC analysis after the metal catalyzed THC oxidation, THCHP and all of the THCHP degradation products previously mentioned are present. Apparently the presence of the Cu and Fe complexes catalyze the formation of THCHP via a nonperoxyl radical chain mechanism.

In Table 1 is reported the effect of addition of two copper deactivators upon the rate of the copper catalyzed THC oxidation. Both deactivators result in a suppression in the rate of oxidation. For instance, in the presence of the better deactivator, N,N'-bis(salicylidene)1,2-diaminopropane, the rate of THC oxidation is about 1/3 of rate in the absence of this deactivator.

We wish to report the following additional observations on the $Fe(acac)_3$ and $Cu(O_2CCH_2CH_2CH_2C_6H_{11})$ catalyzed THC oxidation:

i) Table 2 and 3 reveal the metal catalyzed THC oxidation can occur even when a large concentration of a CB-D antioxidant is present. This observation suggests the mechanisms for these reactions doesn't involve a classical peroxyl radical chain.

ii) In addition, Table 2 and 3 reveal a different rate response in the presence of different concentrations of a CB-D antioxidant. This suggests that the mechanisms for the iron and copper catalyzed oxidations are different.

iii) In Table 4 the rate of a typical copper catalyzed THC oxidation is compared with the rate of an identical reaction in which some tetrahydrocarbazole hydroperoxide (THCHP) was added at the start of the reaction. The observation of similar rates for these reactions additionally suggests that the mechanisms for this reaction is not a classical peroxyl radical chain (lack of chain-branching).

iv) In Table 5 is reported rate data for THC oxidation, as function of THC concentration and metal complex concentration. This data suggests the iron catalyzed reaction is first order in THC and .1 order in iron while the copper oxidation is 1/2 order in THC while .3 order in copper.

CONCLUSION

Pedley et al.[2] have proposed a mechanism which accounts for the involvement of indoles in the formation of sediment and color bodies during ambient aging of an unstable North Sea derived diesel fuel containing catalytically cracked stock. In this mechanism, indoles in the presence of conjugated ketones and acid, result in electrophilic aromatic substitution of the indole with concomitant increase in indole molecular weight and color body formation owing to formation of indolic chromophore. Protonation of the resultant indole results in sediment formation.

The results of this work suggest that alkylindoles can promote fuel degradation in a capacity other than that observed by Pedley et al.[1,2] In the presence of trace amounts of $Fe(acac)_3$ and $Cu(O_2CCH_2CH_2CH_2C_6H_{11})$, tetrahydrocarbazole is oxidized, initially forming tetrahydrocarbazole hydroperoxide (THCHP). A very high concentration of Vitamin E was necessary to completely inhibit the Cu catalyzed reaction while the Fe catalyzed reaction was not totally inhibited.

We have shown that in the absence of catalytically active metal ions and in the presence of CB-D antioxidant THC is oxidatively stable. This observation suggests that more efficient metal deactivators need to be developed in order to counter the effect of alkylindole oxidation upon middle distillate degradation.

LITERATURE CITED

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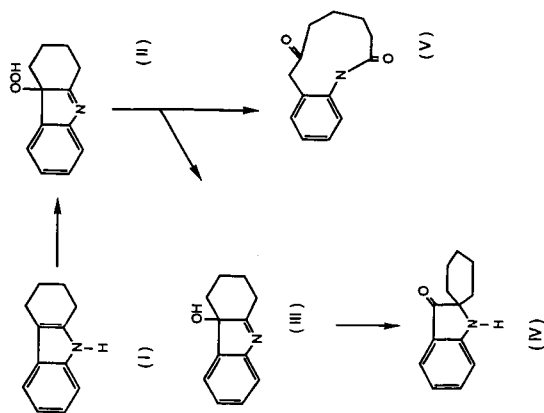9. Witkop, B. and Patrick, J.B., J. Am. Chem. Soc., 73, 2196-2200, (1951).

Table 1*

Effect of N,N bis[salicylidene]1,3-propanediamine and N,N'-disalicylidene-1,2-propanediamine on the Rate of THC Oxidation

Conditions: 2.34×10^{-2} M THC; 2.34×10^{-2} M vitamin E; 50°C; 9.95×10^{-5} Cu2+ cyclohexane butyrate; 50mls 3:1 Heptane-Toluene

MDA	Equivalents of Salicylidene (wrt Cu2+)	rate (moles/1 min) (E^{-6})
1,3	0	10.4
1,3	1.0	5.6
1,3	1.5	5.5
1,2	0	10.4
1,2	1.5	2.8

*Solutions of purified THC, vitamin E, metal and tridecane (GLC internal standard) were prepared in the appropriate solvent mixtures. The solutions were placed in a constant temperature water bath and bubbled with O_2. Aliquots were taken prior to O_2 bubbling and approximately two hours after bubbling. The aliquots were analyzed for THC decomposition using GLC.

FIGURE 1

Table 2

Relationship between Vitamin E Concentration and the Rate of THC Oxidation

conditions:
2.23×10^{-2} M THC/ 1.42×10^{-4} M Fe3+acac/ 50°C/ 50mls 3:1 Heptane-Toluene

Vitamin E (moles/l)	rate (moles/l min) (10^{-6})
0.58×10^{-2}	17.0
1.16×10^{-2}	10.9
2.34×10^{-2}	7.1
4.67×10^{-2}	5.9
9.34×10^{-2}	4.8
14.01×10^{-2}	4.0

Table 3

Relationship between Vitamin E Concentration and the Rate of THC Oxidation

conditions:
2.34×10^{-2} M THC/ 1.99×10^{-5} M Cu2+(cyclohexane butyrate)/40°C/ 50mls 3:1 Heptane-Toluene

Vitamin E (moles/l)	rate (moles/l min) (10^{-6})
1.16×10^{-2}	121.0
2.34×10^{-2}	8.34
4.67×10^{-2}	9.55
7.00×10^{-2}	9.23
9.34×10^{-2}	NR
11.67×10^{-2}	NR
16.35×10^{-2}	NR

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Table 4

Effect of the addition of THCHP on the rate of THC oxidation

conditions:
2.34×10^{-2} M THC/ 1.99×10^{-5} M Cu2+(cyclohexane butyrate)/ 40°C
/ 50mls 3:1 Heptane-Toluene/ 2.34×10^{-2} M vitamin E

THCHP (mg)	rate (moles/l min) (10^{-6})
0 (control)	8.34
10	8.42

Table 5

Determination of Order in THC and Metal

Determination of order in THC with Fe3+acac

Conditions: 1.0 eq. Vitamin E (wrt THC) ; 1.41×10^{-4} M
               Fe3+acac ; 50°C ; 50mls 3:1 heptane –toluene

THC (moles/l)	rate (moles/l min) (E-6)
0.58×10^{-2}	1.55
1.16×10^{-2}	4.1
1.75×10^{-2}	5.5
2.34×10^{-2}	7.1
4.68×10^{-2}	12.6
7.01×10^{-2}	15.4

Table 5

Determination of order in Fe3+acac

Conditions: 2.34×10^{-2} M THC; 2.34×10^{-2} M Vitamin E ;
              50° C ; 50mls 3:1 heptane -toluene

Fe3+acac (moles/l)	rate (moles/l min) (E-6)
2.83×10^{-5}	5.9
1.41×10^{-4}	7.1

Determination of order in THC with Cu2+ cyclohexane butyrate

Conditions: 1.0 eq. Vitamin E (wrt THC) ; 9.95×10^{-5} M Cu2+
            cyclohexane butyrate; 50° C ; 50mls 3:1 heptane -
            toluene

THC (moles/l)	rate (moles/l min) (E-6)
1.16×10^{-2}	6.75
2.34×10^{-2}	9.65

Determination of order in Cu2+ cyclohexane butyrate

Conditions: 2.34×10^{-2} M THC; 2.34×10^{-2} M Vitamin E ;
              50° C ; 50mls 3:1 heptane -toluene

Cu2+ (moles/l)	rate (moles/l min) (E-6)
1.99×10^{-5}	6.9
4.97×10^{-5}	9.7
9.95×10^{-5}	10.6
19.89×10^{-5}	14.0